ALS-lab

Modern Physics, SH1012

2015-04-23

Isak Stomberg, 940210-7271
Robert Vedin, 890814-7831

Atomic Laser Spectrography, laboration in the Course Modern Physics, SH1012, KTH.

ABSTRACT

As a part of the Course Modern Physics, SH1012, held at KTH, students are required to conduct two laboratory exercises, of which ALS is one.

The purpose of the lab is to see a real-world example of the quantization of vibrational states as well as get some hands on experience in the field of spectroscopy.

Specifically the assignment is to use the spectroscopy equipment to determine the Morse potential function of the molecular iodine $I^2 X^1\Sigma$ ground state.

In the lab, a HeNe 543.5 nm laser were used to excite vibrational states of iodide molecules. When transitioning back to lower excited levels, characteristic photons are emitted. This light were detected and split into peaks using the spectrograph, and then analysed to obtain desired results such as the constants in the morse potential. Also vibrational constants were determined.

The lab was successfully conducted and hence the Morse potential determined for iodine. Some aspects of the implementation are discussed combined with a brief comparison of results with reliable sources. Some deviations were present, but considering the instrumental qualities and other affecting factors, we are content with the overall outcome.

NOMENCLATURE

Symbol	Description, [unit]
D_e	Dissociation energy, $[cm^{-1}]$
r_e	Equilibrium interatomic distance in molecule, $[\text{Å}]$
r	Interatomic distance in molecule, $[\text{Å}]'$
ω_e	Rotational constant, $[cm^{-1}]$
$\omega_e x_e$	Rotational constant, $[cm^{-1}]$
σ	Wave number, $[cm^{-1}]$
$\Delta\sigma$	Difference in wavenumber between two adjacent lines, $[cm^{-1}]$
λ	Wavelength of the emitted light, $[nm]$
a	Morse potential constant, $[\text{Å}^{-1}]$
h	Plancks constant, $[Js]$
c	Speed of light, $[ms^{-1}]$
ν	Vibrational quantum number in ground state, $[Dimensionless]$
υ	Vibrational quantum number in second electron state, $[Dimensionless]$
f	Photon frequency, $[s^{-1}]$
μ	Reduced mass, $[kg]$

1 INTRODUCTION

Background and Purpose

As a part of the Course Modern Physics, SH1012, held at KTH, students are required to conduct two laborations exercises, of which ALS is one.

The purpose of the lab is to obtain an overall insight into the field of laser spectrography and to get hands experience with modern methods for spectrographic analysis used in atomic, molecular and chemical physics. More explicitly, the objective of the exercise is to determine molecular vibrational constants and the Morse potential function for molecular iodine, $I_2 X^1\Sigma$, ground state.

2 THEORY

2.1 General Ideas

In molecular physics and quantum mechanics, different excitation states of molecules are explained and studied. For example vibrational states, which are the ones studied in this lab. These states can be exited by certain photon wavelengths, corresponding to the quantized energy differences between these states. Light from a NeHe 543.5 nm laser coincide with the transition $I_2 X^1\Sigma$ ground state to $B^3\Pi_0$ of molecular iodide, I_2. That is, the laser will cause a transition from the ground state to the 26:th vibrational level of the second electron-excited state. As a consequence, the molecule will undergo different downward transitions toward lower energy levels, emitting photons corresponding to the energy differences, until ground state is again reached. These may be detected and observed using spectroscopic methods, one of which is used in this lab. The result is a characteristic spectrum consisting mainly of different peaks in the number of detected photons for certain wavelengths.

2.2 Formulas and useful results

Variables and constants not commented under each subtitle are as given in the Nomenclature.

To describe the shared potential of atoms in a two-atomic molecule, the morse potential is a good approximation. It is given by the equation

$$V(r) = D_e \left[1 - e^{a(r_e - r)} \right]^2. \qquad (1)$$

Solving the Schrödinger equation for the morse potential, yields the quantized vibrational energy levels E_v, and the expression $G(v) \sim E_v$ according to

$$G(v) = \frac{E_v}{hc} = \omega_e(v + 1/2) + \omega_e\chi_e(v + 1/2)^2 + \omega_e y(v + 1/2)^3, \ v = 1, 2, 3.... \tag{2}$$

For the excited state $\upsilon = 26$, we have the energy equation (with different constants)

$$F(\upsilon) = T_e + \omega'_e(\upsilon + 1/2) + \omega_e\chi'_e(\upsilon + 1/2)^2 + \omega_e y'(\upsilon + 1/2)^3, \upsilon = 1, 2, 3... \tag{3}$$

Thus, for an deexcitation from the $\upsilon = 26$ to a v vibrational state, we can write the wavenumber σ for an emitted photon according to

$$\sigma = \sigma_v = 1/\lambda_v = f_v/c = f_v h/ch = \Delta E/hc = F(\upsilon = 26) - G(v). \tag{4}$$

Hence, we end up with

$$\Delta\sigma = \sigma_v - \sigma_{v+1} = G(v + 1) - G(v). \tag{5}$$

Define now

$$\Delta G(v + 1/2) = G(v + 1) - G(v). \tag{6}$$

Using equation (2) and ignoring higher order terms since $\omega_e\chi_e$ is small compared to ω_e, we end up with the approximation

$$\Delta G(v + 1/2) = G(v + 1) - G(v) = \omega_e - 2\omega_e\chi_e - 2v\omega_e\chi_e. \tag{7}$$

We wish to determine the vibrational constants in equation (7). But since σ_v is observed in the lab and the validity of equation (5), one conclude that

$$\sigma_v - \sigma_{v+1} = G(v + 1) - G(v) = \omega_e - 2\omega_e\chi_e - 2v\omega_e\chi_e \tag{8}$$

is a linear equation in v. Therefore, plotting the observed differences $\sigma_v - \sigma_{v+1}$ as a function of v, an estimate of ω_e and $\omega_e\chi_e$ can be made. Summing $\Delta G(v + 1/2)$ for all v, we end up with a number that in our case is approximately equal to D_e. It is possible to show that after doing the summation, the result is:

$$D_e = \frac{\omega_e^2}{4\omega_w\chi_e} \ . \tag{9}$$

We now want to relate $\omega_e\chi_e$ to a. After some math, and taking the derivatives of the Morse potential, one get the following relationship:

$$\omega_e\chi_e = \frac{hq^2}{8\pi^2 c\mu}. \tag{10}$$

Furthermore, from literature, we knows that

$$B_e = \frac{h}{8\pi^2 c\mu \cdot r_e^2} \ .$$
(11)

Now, after conducting the lab, and using equations (9), (10) and (11) together with the obtained values for ω_e and $\omega_e \chi_e$, one have all relations needed to deduce the constants in Morse potential.

Other useful formulae are

$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$
(12)

where m_1 and m_2, in this case, are taken as equal to the mass of the iodine atom,

and Bragg's law, describing the self interference of light reflected in a crystal-like surface. The phenomenon can be modeled as light being reflected in different atomic planes, causing it to self interfer. When the phase shift is equal to an integer n times the wavelength, constructive interference occurs, as described by bragg's law

$$n\lambda = 2d\sin(\theta)$$
(13)

where n is an integer, d the atomic layer distance in the surface and θ the angel of the incoming light relative to the surface.

3 IMPLEMENTATION

3.1 Materials

Equipment used: 543.5 nm HeNe laser
Test cell containing iodide, I_2
Focusing lens
Monochromatic Hg filters
Spectrometer
Analysing computer
White light

3.2 Experimental Setup

The laser was directed at the iodide cell. The light emitted from the cell was focused into the spectrometer (monochromator) whose output was sent to and graphically presented on a computer screen. See figure 1 for a schematic view of the setup configuration. Further details are given in section 3.3.
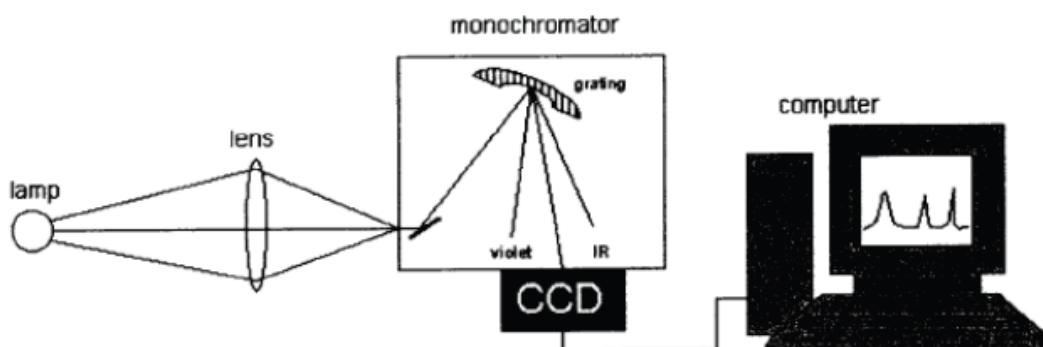
Figure 1. Schematic view of the experimental setup configuration.

3.3 Method and conduction

We started by calibrating the spectrometer, using a mirror and a lens to direct the light from a roof lamp. Monochromatic Hg filters were thereafter placed in the light's path. Data output in the computer were given in plots with y-axis Numbers detected photons and x-axis Channel number. Knowing the transmitted wavelength let us relate that particular wavelength to the corresponding channel number. Plotting the wavelength against the channel number we approximately get a line. With the data from result: table 1 we can then make a least square fit to determine the equation of the line and thus the equation that relates the recorded channel number to the wavelength of the detected light. According to bragg's law, and since the spectrometer use reflection in a crystalline-like structure, an extra peak in the plot output was seen. Because this peak is recorded at the same channel as would a peak from light with wavelength 2λ

$$2dsin(\theta_2) \ = \ 2 \cdot \lambda = 1 \cdot (2\lambda) \ = \ 2dsin(\theta'_1)$$

we can consider this an extra reference wavelength whose first diffraction peak is recorded at angle θ'_1. To govern a more precise curve fit, these peaks were added to the table, with wavelength corresponding to twice the wavelength transmitted through the filter, according to bragg's law.

Once we had a calibration equation, we put the iodine cell below the laser and used the same lens to direct the emitted light into the spectrometer (monochromator). To get a good result we used background subtraction to set a new baseline taken as the average of 50 spectra. The laser were turned on, which caused the excitation of iodide molecules to the state $B\,^3\Pi_0$, and thereafter transitions to different vibrational states of the electron ground

state. With background noise removed, a relatively clear spectra were obtained as the average of 50 spectra. Peaks were identified and recorded, see result: table 2.

4 RESULT

4.1 Calculations and derived equations

Calibration of experimental setup
The calibration equation has the form $\lambda = \alpha k + \beta$, where k is taken to be the (dimensionless) channel number. The least square fit of the parameters can be seen in figure 2, using the data from table 1, is $\alpha = 5.2767 \, [\text{Å}]$ and $\beta = 808.3531 \, [\text{Å}]$
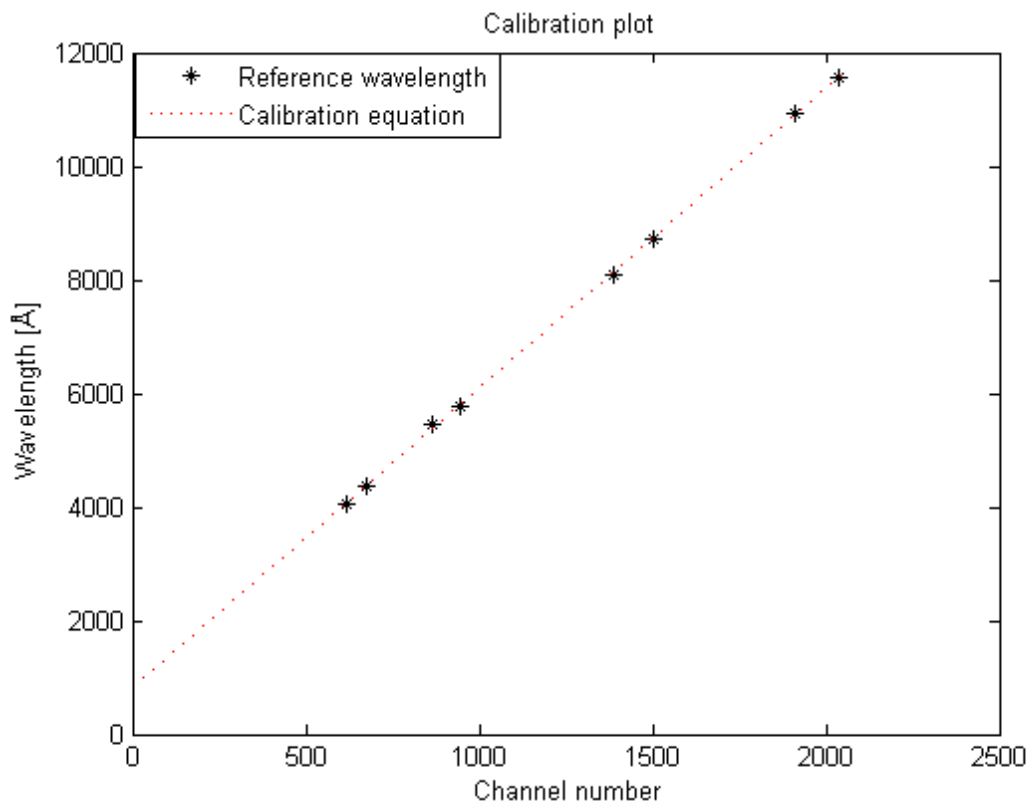

Figure 2. Plot of the data as well as a least square fit of the calibration equation.

Linear Birge-Spooner extrapolation

To determine the vibrational constants ω_e and $\omega_e\chi_e$ we do a least square fit to the linear Birge-Spooner extrapolation where $\Delta\sigma_v = \sigma_v - \sigma_{v+1} = \omega_e - 2\omega_e\chi_e - 2v\omega_e\chi_e$.

Figure 3 shows our measured values of $\Delta\sigma_v$ plotted against the quantum numbers v as well as the least square fit to the function above. This gives us the values of the vibrational constants $\omega_e = 0.6823\ [cm^{-1}]$ and $\omega_e\chi_e = 210.5486\ [cm^{-1}]$.
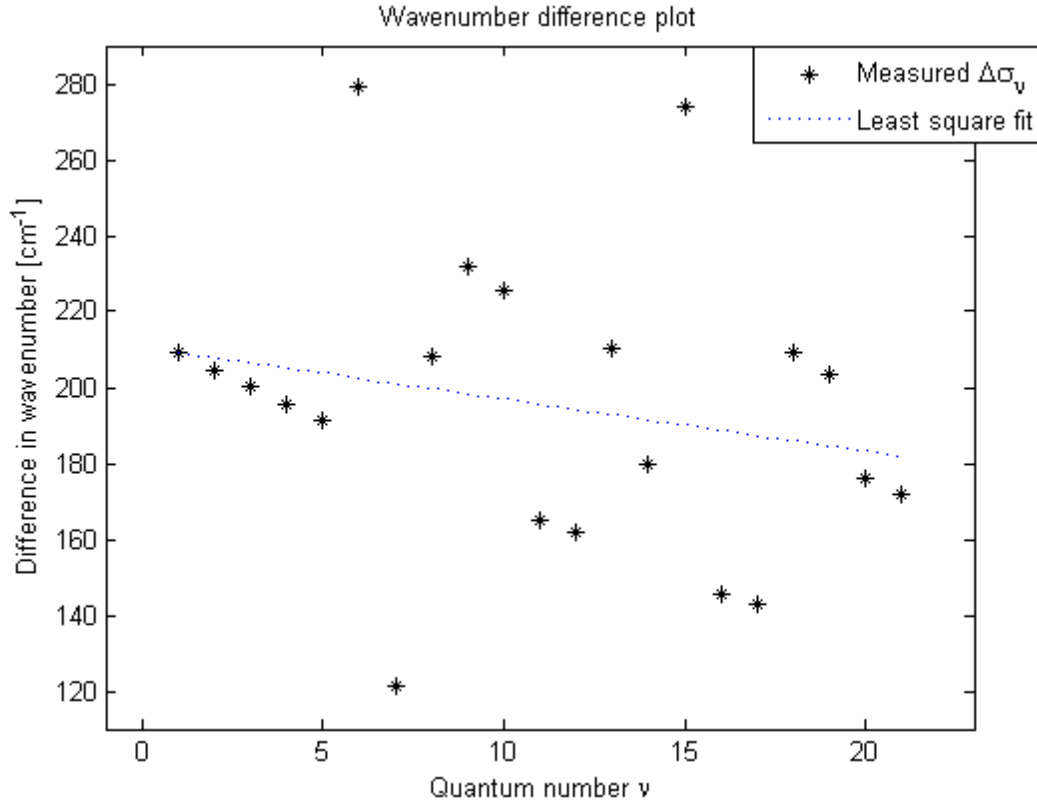

Figure 3. This plot shows the difference in wavenumber $\Delta\sigma_v$ plotted against the quantum numbers v as well as the least square fit to a linear Birge-Spooner extrapolation.

Morse potential

Now that we have calculated the vibrational constants, see table 3, we can use the provided equations to calculate the constants needed to define the Morse potential.

From eq. (9) we get

$$D_e = \frac{\omega_e^2}{4\omega_e\chi_e} \simeq 16242\ [cm^{-1}] \tag{14}$$

and from eq (10)

$$a = \sqrt{\frac{\omega_e\chi_e 8\pi^2 c\mu}{h}} \simeq 1.6023 \cdot 10^9\ [dm^{-1}] = 1.6023\ [1/\text{Å}] \tag{15}$$

lastly from eq (11) we get

$$r_e = \sqrt{\frac{h}{8\pi^2 c \mu B_e}} \approx 2.667 \cdot 10^{-9} \, [dm] = 2.667 \, [\text{Å}] \tag{16}$$

In figure 4 we have plotted the Morse potential $V(r) = D_e(1 - e^{a(r_e - r)})^2$, with the parameters as written above, as a function of the interatomic separation r.
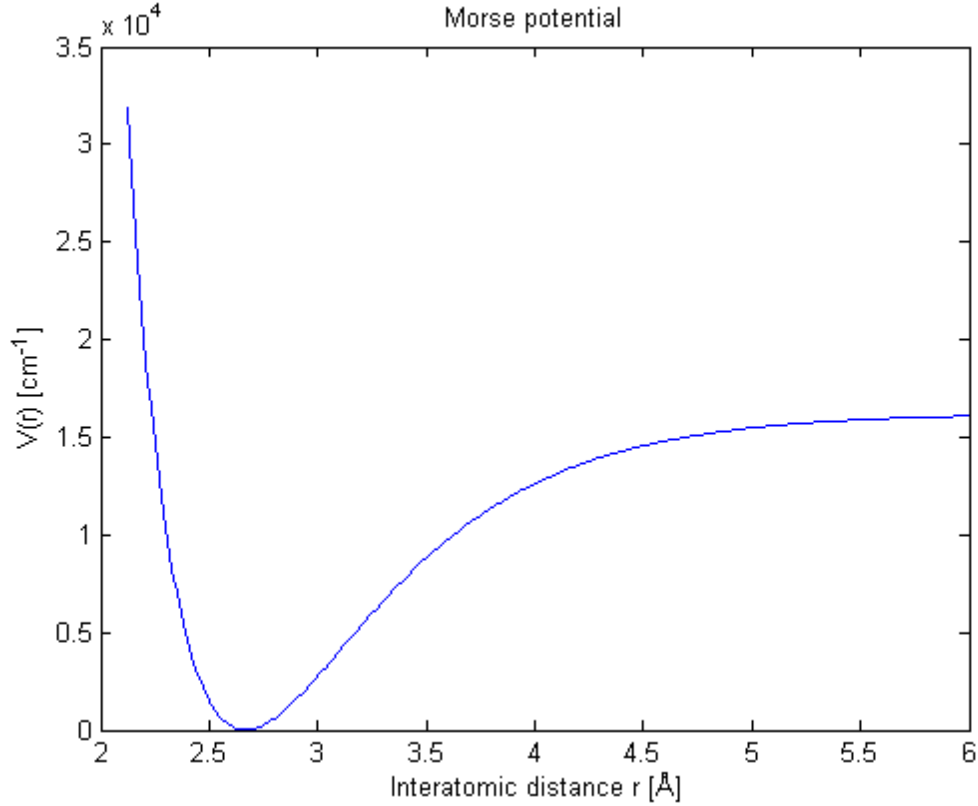

Figure 4. A plot of the morse potential using the deduced parameters.

Interpolated wavenumbers

Our spectrum was not clear enough to be able to discern every peak, however since we expect the energy to be a linear function of the quantum number v and the channel number a linear function of the energy we also expect the peaks to be evenly spaced. Using this, we see in the plot that between some of the peaks, another is expected. Below is a method for interpolation of these peaks described.

Taking the difference between $\Delta\sigma_v$ for two consecutive v we get a relation between the peak wavelengths that will let us interpolate the location of a peak that we can not see:

$$\Delta(\Delta\sigma_v) = \Delta\sigma_v - \Delta\sigma_{v+1} = (\omega_e - 2\omega_e\chi_e - 2v\omega_e\chi_e) - [\omega_e - 2\omega_e\chi_e - 2(v + 1)\omega_e\chi_e] = 2\omega_e\chi_e$$

9

Keeping in mind that $\Delta\sigma_v = \lambda_v^{-1} - \lambda_{v+1}^{-1}$ we can now write

$$\Delta(\Delta\sigma_v) = \lambda_v^{-1} - 2\lambda_{v+1}^{-1} + \lambda_{v+2}^{-1} = 2\omega_e\chi_e \qquad (17)$$

Because we know that the vibrational constant $\omega_e\chi_e$ is really small compared to the wavenumbers, we omit it, and get the approximate relation between the wavelengths

$$\lambda_{v+1} \simeq 2\lambda_v\lambda_{v+2}(\lambda_v + \lambda_{v+2})^{-1} \qquad (18)$$

which we can use to interpolate the peaks that can not be seen in our own spectrum.

4.2 Tables

Table 1:

Wavelength [Å]	4047	4358	5461	5780	8094	8716	10922	11560
Channel number	617	673	867	947	1387	1505	1913	2035

Wavelength of the filtered light in the calibration setup.

Table 2:

Peak number	1	2	(3)	4	(5)	6	7	8	(9)	10	(11)
Channel number	883	895	907	919	931	943	961	969	983	999	1015
λ [nm]	547	553	559	565	572	578	587	592	600	608	616
$\sigma\,[cm^{-1}]$	18289	18080	17875	17675	17480	17288	17009	16888	16680	16448	16223
$\Delta\sigma\,[cm^{-1}]$	209	205	200	196	191	279	121	208	232	225	165

Peak number	12	13	14	15	16	17	(18)	19	(20)	21	22
Channel number	1027	1039	1055	1069	1091	1103	1115	1133	1151	1167	1183
λ [nm]	623	629	638	645	657	663	669	679	688	697	705
$\sigma\,[cm^{-1}]$	16058	15896	15686	15506	15232	15086	14943	14734	14531	14355	14183
$\Delta\sigma\,[cm^{-1}]$	162	211	180	274	146	143	209	203	176	172	

The channel where the peaks were recorded starting from the shortest wavelength, bracketed peaks are interpolated using equation 18. Note that peak number n correspond to a transition to the quantum number $v = n - 1$.

Table 3:

$B_e\ [cm^{-1}]$	$\omega_e\ [cm^{-1}]$	$\omega_e\chi_e\ [cm^{-1}]$	$D_e\ [cm^{-1}]$	$a\ [Å^{-1}]$	$r_e\ [Å]$
0.03737	210.5486	0.6823	16242	1.6023	2.667

The calculated vibrational constants as well as the parameters for the Morse potential.

5 DISCUSSION AND CONCLUSIONS

5.1 Discussion

Overall we are satisfied with our results, however there are a few things that did not go quite the way we expected them to.
Firstly the calibration, as became evident later on our calibration of the spectrometer had not been ideal. Given that we knew that the wavelength of the laser should coincide with the energy of the vibrational level u = 26 of the excited state $B^3\Pi_0$ of the iodine sample we would have expected to register our first peak at the channel corresponding to that wavelength however that was not what the spectrometer showed. We think this discrepancy is likely caused by the difference in the angle of the incident light during the calibration, when we used a mirror to direct the light into the spectrometer, and during the data collection when the light source was right in front of the spectrometer.This inconsistency in angles caused the latter light to undergo and observed phase-shift compared to the expected phase (channel) for 543.5 nm.

We had to interpolate the expected wavelength for some peaks. This would not be appropriate for a more sophisticated and rigorous experiment, however, since the theory governing the principles of this lab is well supported by other experiments, we could allow ourselves to use interpolation methods, in order to fill certain holes.

It should be commented that we have not taken into account rotational transitions. This is simply because they cannot be observed. The resolution of the instruments used is good enough to resolve the different vibrational transitions, but since rotational transitions are much less energetic, they are not resolvable, and hence pass invisible to us.

In the calculation of D_e we use the Birge-Spooner approximation where D_e is approximately equal to D_0. Because the energy difference between two vibrational states

is approximately linear we can estimate the difference is between D_e and D_0 by looking at the difference in energy between the two lowest vibrational states $(\nu = 0,\ 1)$. If the difference between D_e and D_0 were much greater we might expect that a lower ground state were possible. There is no such, and we therefore consider the used approximation to fall within the uncertainty of our measurements. From table 2 we get that our calculated difference between the first two states is $209\ [cm^{-1}]$ and that our calculated D_e is $16242\ [cm^{-1}]$. Since the difference 209 is so much smaller than 16242 we consider the approximation of D_e to be reasonable.

A perfect setup configuration was critical in order to achieve a detailed spectrum. Exact alignment with the laser, lens spectrometer and very good focus were necessary to obtain satisfying result. We concluded during the lab that we could have done a better job here, but since we were able to discern a sufficient amount of peaks, we found ourselves content.

5.2 Conclusions

To compare our results we were able to find a report (see reference 1) published from the LaSalle University, Philadelphia about a similar experiment. Our experimental results, as seen in table 3, for the parameters in the Morse potential match up fairly well with ones we found in their report:

$D_e\ [cm^{-1}]$	$r_e\ [\text{Å}]$	$a\ [\text{Å}^{-1}]$
18941	2.66	1.517

Given that our results match so well (within a factor 2) we are confident that the parameters we have found will provide a reasonable approximation for the Morse potential function of the I_2 molecule.

6 REFERENCES

[1] Report from the LaSalle University, Philadelphia regarding Vibronic Spectra of Diatomic Molecules and the Birge-Sponer Extrapolation

http://users.auth.gr/akrivos/Physices%20Methodoi/diatomic%20vibronic%20spectra.pdf

.